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Advances in Acid Concentration Membrane Technology for the Sulfur-Iodine Thermochemical Cycle

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Advances in Acid Concentration Membrane Technology for the Sulfur-Iodine Thermochemical Cycle

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Abstract

One of the most promising cycles for the thermochemical generation of hydrogen is the Sulfur-Iodine (S-I) process, where aqueous HI is thermochemically decomposed into H_2 and I_2 at approximately 350 ^oC. Regeneration of HI is accomplished by the Bunsen reaction (reaction of SO_2, water, and iodine to generate H_2SO_4 and HI). Furthermore, SO_2 is regenerated from the decomposition of H_2SO_4 at 850 ^oC yielding the SO_2 as well as O_2. Thus, the cycle actually consists of two concurrent oxidation-reduction loops. As HI is regenerated, co-produced H_2SO_4 must be separated so that each may be decomposed. Current flowsheets employ a large amount (~83 mol% of the entire mixture) of elemental I_2 to cause the HI and the H_2SO_4 to separate into two phases. To aid in the isolation of HI, which is directly decomposed into hydrogen, water and iodine must be removed. Separation of iodine is facilitated by removal of water.

Recent efforts at the INL have concentrated on applying pervaporation through Nafion-117, Nafion-112, and sulfonated poly(ether ether ketone) (SPEEK) membranes for the removal of water from HI/water and HI/Iodine/water feedstreams. In pervaporation, a feed is circulated at low pressure across the upstream side of the membrane, while a vacuum is applied downstream. Selected permeants sorb into the membrane, transport through it, and are vaporized from the backside. Thus, a concentration gradient is established, which provides the driving force for transport. In this work, membrane separations have been performed at temperatures as high as 134 ^oC. Transmembrane fluxes of water are commercially competitive (~5000 g/m^2h) and separation factors have been measured as high as 8000, depending on the membrane and the water content. For the Nafion-117 experiments, the common trade off in membrane performance is observed in that as flux is increased, separation factor decreases. Nafion-112, a thinner membrane, exhibited much higher fluxes than the Nafion-117 without loss in separation factor. All membranes exhibited no degradation in membrane performance during use.

Pervaporation was also applied with similar results for the concentration of sulfuric acid. Decomposition of sulfuric acid is equilibrium limited requiring a recycle stream. Concentration by distillation involves serious corrosion issues at the vapor-liquid interface. In this work, Nafion-112® was used successfully as a membrane to remove water from sulfuric acid using pervaporation.

Introduction

Thermochemical water splitting cycles are methods that have been proposed to generate hydrogen on a commercial scale. In general, hydrogen today is formed from the steam reforming of natural gas. Hydrogen generated using this method is consumed in

industrial processes, such as petroleum refining. Interest exists in using hydrogen as an energy carrier for the transportation energy sector and other applications where petroleum is used today.

Formation of hydrogen from thermochemical cycles has been proposed using nuclear reactor supplied thermal energy.[1] The only chemical input is water and the only effluent is oxygen and hydrogen. From an energy input standpoint, heat, in the range of 750 °C to 1000 °C, is provided to drive the reactions, which tend to be endothermic. Thermochemical cycles were principally investigated from the 1960's through the 1980's. However, interest waned with the drop in crude oil prices in the 1980's. Recent energy price increases and U.S. national security issues have renewed interest in hydrogen production. Advantages of nuclear driven hydrogen production include hydrogen's inherent renewable nature, a reliance of the process on U.S. domestic resources, and an absence of CO_2 emissions. Similar advantages can be obtained through the use of high temperature solar concentrators.

In the literature, more than 100 thermochemical cycles have been proposed and studied to some degree.[2] One of the more developed cycles, the sulfur-iodine process (S-I), [3], is comprised of three chemical reactions. Water enters the cycle as a reactant in the Bunsen reaction[4], as shown in Eq 1.

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \qquad \text{Eq 1}$$

In Eq.1, hydriodic acid (HI) is formed from the reduction of I_2 at an approximate temperature of 120 °C. HI is then decomposed to generate H_2 at 400 °C, Eq.2, and the co-generated I_2 is recycled. To re-generate SO_2, H_2SO_4 is decomposed at temperatures as high as 900 °C, Eq 3.

$$2HI \rightarrow H_2 + I_2 \qquad \text{Eq 2}$$

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2 \qquad \text{Eq 3}$$

Key to the operation of this proposed cycle is the Bunsen reaction. Current flowsheets indicate that 7500 Kg of material must be physically moved within a plant for every Kg of hydrogen generated, and much of this mass is iodine associated with the Bunsen reaction. A large excess of I_2 is added to separate the HI from the H_2SO_4, which causes the product mixture to separate into two phases. Water and H_2SO_4 comprise the lighter phase, while the heavier phase is a mixture of HI, water, and I_2 at an approximate ratio of 2:10:8:, respectively. To facilitate this phase separation, a dehydration loop employing concentrated phosphoric acid has been proposed to be added to the system to remove water from the HI/I_2 mixture. Direct removal of water using a membrane process would allow for a large reduction in the amount of iodine, thus increasing the efficiency of the cycle by lowering the recycle ratio per Kg of hydrogen generated. However, membrane concentration of HI/I_2 mixtures has not been demonstrated. For these studies, we have focused on Nafion-117®, Nafion-112®, and sulfonated poly(ether ether ketone) (SPEEK) membranes in the pervaporation of water from an HI/water, HI/water/I_2 feed and a sulfuric acid feed.

Experimental Methods

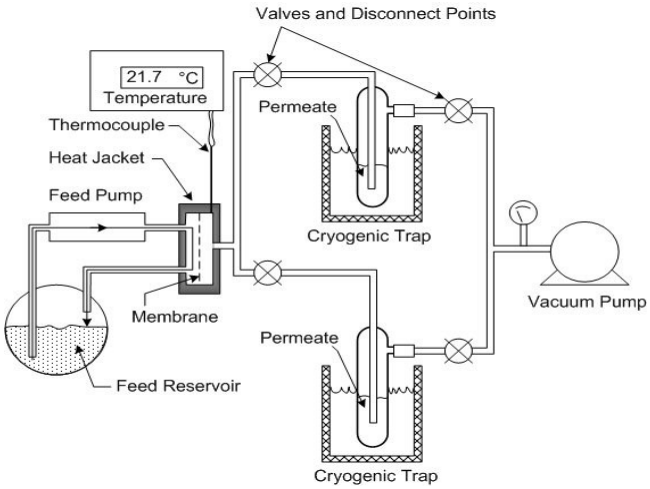

Figure 1. Pervaporation System

Nafion-117® and Nafion-112® membranes were obtained from Aldrich Chemical Co.[5] and used as received. Membrane thicknesses were measured using a Mitutoyo micrometer to be approximately 180 μm and 50 μm for Nafion-117® and Nafion-112®, respectively. Sulfonated poly(ether ether ketone) (SPEEK) was prepared by the method of Huang[6] and solution cast from DMSO into membranes that were dried at 160 ^{o}C in a vacuum oven prior to use. The HI/iodine feed was prepared by addition of deionized water (40 g) and elemental iodine (100.9 g, Aldrich Chemical Co.) to a 55 % aqueous solution of HI (86.9 g, Aldrich Chemical Co.). The HI feed consisted of the 55 % HI as received without dilution. HI concentrations in both the feed and permeate samples were determined by titration against standardized sodium hydroxide solutions to a phenolphthalein endpoint. A pervaporation apparatus, Fig. 1, was constructed for this work using a Millipore 47 mm filtration cell modified with an extra port for feed side flow.

Membranes were secured using Viton O-rings and leak-checked against 50 psi nitrogen gas prior to use. All tubing and connectors were made of Teflon®. Pumping of the feed was accomplished using a Teflon® or Viton® rubber peristaltic pump obtained from Cole-Parmer Inc. Temperatures were measured at the cell using a calibrated thermocouple. The temperature of the cell was controlled with heat tape. Feed flow rates were sub-turbulent at approximately 10-30 ml per minute. Permeate side pressure was maintained at 100 mTorr using a mechanical vacuum pump. All permeates were trapped cryogenically and measured gravimetrically to determine the transmembrane flux.

Results and Discussion

HI and HI/Iodine Concentration. Nafion-117® is a commercially available perfluoroethylene sulfonate membrane with an ion exchange capacity of 1100 g/EW (grams per equivalent weight) and a thickness of 0.007" (180 μm). It is a durable plastic material that is easy to install into a pervaporation system. However, its structure is far more complex with a porous, phase-separated nature that results in both hydrophilic and hydrophobic regions. The hydrophobic portions of the polymer consist of Teflon-like

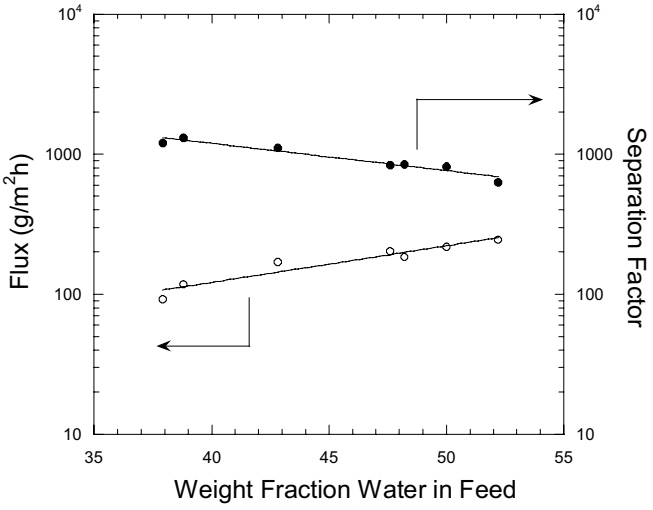

Figure 2. Nafion-117 membrane performance at 134 ºC (HI feed).

perfluoroethylene units, while the hydrophilic sulfonates, which are attached to the polymer backbone through perfluorinated chains, tend to form inverse micelles giving tortuous pathway pore structures through which water can pass.

Testing of Nafion-117® membranes was conducted at 134 °C as shown in Figure 2. Chronologically, the plot is read right to left where the concentration of water was reduced. Both fluxes and separation factors were determined using an HI/water feed. Flux of water ranged from 92 – 245 g/m^{2}h and decreased with increasing HI concentration, which also corresponds with decreasing water concentration. Separation factors ranged from 633 – 1208, which are commercially competitive. With respect to increasing HI concentration, fluxes were observed to decrease and separations factors increased. This behavior is typical of membrane processes in which a trade-off is observed between flux and separation factor. Decreasing fluxes with decreasing water concentration also is typical of membrane processes. It should also be noted that the acid has been concentrated beyond the azeotrope of 57% HI (43% water).

Experiments using a HI/water/I_2 feed were found to require a slight re-engineering of the test system. The most significant modification was the replacement of a half of the membrane cell with a Teflon® component. The membrane cells used in this work consist of two halves that are bolted together; a feed side and a permeate side with the membrane mounted as a separator. In this work, the feed side was duplicated by the INL machine shop using a Teflon block. The permeate side was retained because of the rigidity that it provided to the cell as a whole and due to the membrane's ability to perform the separation, the permeate side did not experience any significant corrosion.

HI/iodine concentration experiments were conducted at 134 °C using a feed that consisted of a 1:10:1 molar ratio of HI, water and I_2, respectively. As shown in Figure 3, the data is consistent with the above experiments in which higher fluxes of water are observed from feeds that have a higher water concentration. Fluxes of water range from 242-1353 g/m^{2}h, depending on feed concentration. Separation factors, likewise, were observed to increase with decreasing feed water concentration, ranging from 3875 to 7431. These data are significantly higher than the previous experiments, which could be due to the extremely low concentration of HI/iodine in the permeate. However, the relative difference in separation factors from previous experiments shown above to this experiment should not be considered overly significant due to the mathematical implications of dividing large numbers by small numbers. Slight deviances in the smaller terms, such as permeate HI/iodine concentrations in the 10^{-3} – 10^{-4} range, can cause inordinately large swings in the measured separation factor. The more meaningful conclusion that can be drawn from this experiment is that the permeate of both HI/water and HI/water/I_2 experiments are virtually the same in terms of their composition.

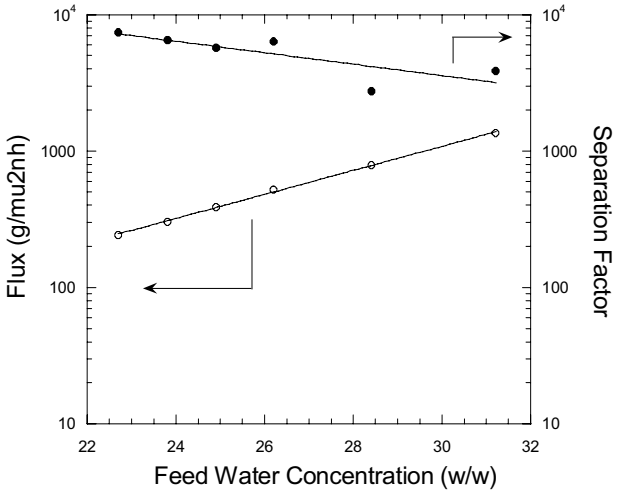

Figure 3. Performance of Nafion-117 in concentrating HI/iodine at 134 ºC.

Nafion-112® has the same equivalent weight of ion carrier as does the Nafion-117®. The only difference is the material thickness. Nafion-112® is substantially thinner at 0.002" (50 μm). Thinner membranes are expected to yield far higher permeant fluxes while maintaining the separation factor. This was of interest because the Nafion-117® membranes performed an effective separation for the S-I process, so a thinner membrane could potentially yield higher fluxes, thus reducing the size of any installed membrane plant, provided the thinner membrane could maintain structural integrity and not degrade under the experimental conditions. Permeant fluxes are directly reflected by the membrane area in that lower flux processes require larger membranes per unit volume of feedstream. Conversely, higher flux processes result in lower membrane area requirements, which, in turn, significantly lower the membrane process capital, operations, and maintenance costs.

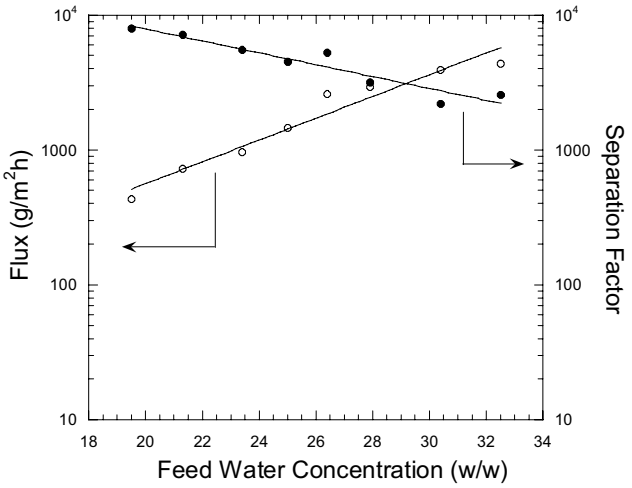

Figure 4. Nafion-112 membrane performance in concentrating HI/iodine at 134 ºC.

At 134 °C, both fluxes and separation factors were measured as shown in Fig. 4. With respect to feed water concentration, the trade-off between flux rate and separation factor was again observed. However, in this instance, the fluxes were far higher as compared to the Nafion-117® experiment, ranging from 431-4353 g/m^{2}h. Higher fluxes were obtained with no loss of separation factor, suggesting that, under the conditions of these experiments, concentration polarization due to a boundary layer was not a factor in the separation.

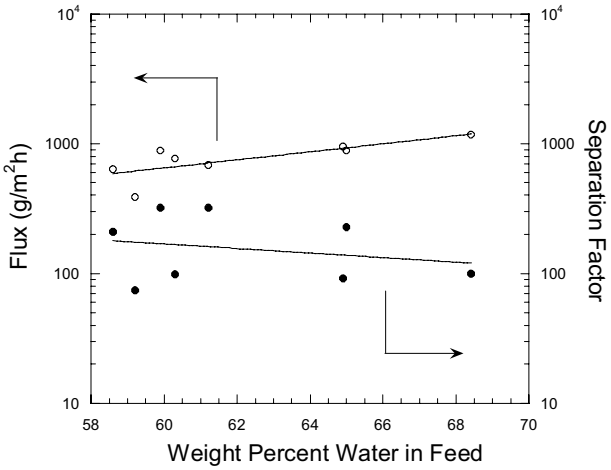

Figure 5. Performance of 1.8 SPEEK for the concentration of HI at 57 ºC.

Sulfonated poly(ether ether ketone) (SPEEK) membranes were also investigated for this separation. The advantage of SPEEK is that it is substantially cheaper and more processable than Nafion® polymers. Preparation of SPEEK membranes first required sulfonation of commercially obtained PEEK. Sulfonation readily occurred by immersion of PEEK in concentrated sulfuric acid (98 %) followed by heating to 68 ºC for controlled periods of time. Longer heating times yield polymers with higher densities of sulfonate groups, which equates to the ion exchange capacity (IEC). Polymers with IECs as high as 2.3 meq/g were found to be soluble in water. At an IEC of ~1.8 meq/g, robust polymers that were soluble in DMSO (for membrane

casting) but insoluble in water were formed. 1.8 SPEEK was measured to swell in water ~25%, comparable to Nafion®, and maintained dimensional stability when swollen.

Membranes of 1.8 SPEEK were prepared by solution casting of a 10 % (w/v) DMSO-polymer solution on to a glass plate preheated to 100 °C on a hotplate. While drying, the membrane was covered to control the solvent evaporation rate. After 3 hours, the membrane was removed from the glass plate and further drying was accomplished using an argon-vacuum oven at 160 °C for 3-4 days. Preliminary data on the performance of the 1.8 SPEEK membranes is shown in Fig.5. In this experiment, the acid was concentrated from 32 % to 42%. As seen with the Nafion® membranes, flux decreases as the concentration of water decreases. The separation factor data has a considerable amount of scatter, from 100-300, that can be attributed to the preliminary nature of the data. A comparison of this data to similar experiments performed on Nafion-117® membranes shows a high degree of correlation.[7]

Sulfuric acid concentration. A natural extension of this work is the concentration of sulfuric acid. In the S-I cycle, sulfuric acid is decomposed to SO_2, O_2, and water. Decomposition of sulfuric acid is an equilibrium limited process accomplished through the use of a catalyst. With limited conversion, undecomposed acid exits the reactor with the decomposition products. With the production of water, the acid concentration of the effluent is lower than that of the feed. A curious note concerning sulfuric acid is that dilute acid is more corrosive than concentrated acid. Thus, to effect a recycle of the undecomposed acid, it must be concentrated. Distillation poses technical difficulties in that corrosion rates are the highest at the vapor-liquid interface. Thus, if concentration could be performed *without* boiling, rates of corrosion could be reduced significantly, which translates into reduced capital and operations costs.

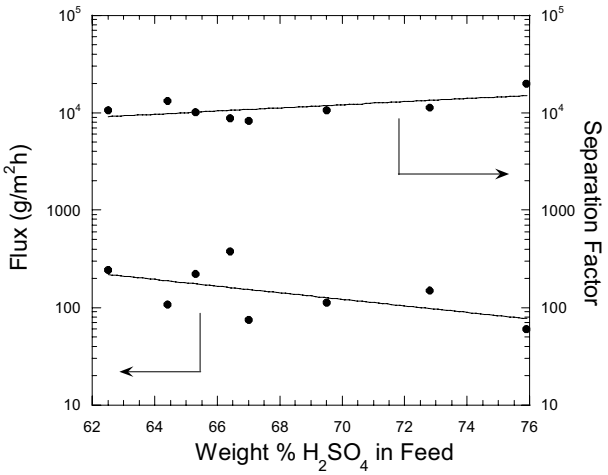

Figure 6. Concentration of Sulfuric Acid using Nafion-112® at 100 ºC.

Both Nafion-117® and Nafion-112® membranes were studied against an aqueous sulfuric acid feed. In an example collected using Nafion-112® at 100 °C, sulfuric acid was concentrated from 62 to 76 %, Fig 6. Fluxes varied from 381 to 60 g/m^{2}h and decreased with increasing acid concentration (decreasing water concentration). Separation factors were quite high, ranging from 8000 to 13000. Also, no degradation of the membranes was observed at these temperatures. Further experiments are on-going to determine the feasibility of long term use of Nafion® membranes for this separation.

Conclusion

Two separate membrane processes relevant to the Sulfur-Iodine cycle were studied with respect to membrane performance and materials compatibility. Nafion® membranes were found to effectively concentrate HI/iodine mixtures at 134 °C. Furthermore, initial data collected using SPEEK membranes for the concentration of HI reveals similar performance as

observed for Nafion®. Nafion® membranes were also found to be effective in the concentration of sulfuric acid. The membranes used in these experiments showed good stability in terms of both transport behavior and physical integrity.

Acknowledgment

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[5] References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho National Laboratory.

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